



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: G01N 31/10, 30/88	A1	(11) International Publication Number: WO 99/60396 (43) International Publication Date: 25 November 1999 (25.11.99)
<p>(21) International Application Number: PCT/FI99/00382</p> <p>(22) International Filing Date: 10 May 1999 (10.05.99)</p> <p>(30) Priority Data: 981088 15 May 1998 (15.05.98) FI</p> <p>(71) Applicant (for all designated States except US): FORTUM OIL AND GAS OY [FI/FI]; Keilaniemi, FIN-02160 Espoo (FI).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): LIPIÄINEN, Kyösti [FI/FI]; Suorannantie 10 B 6, FIN-06450 Porvoo (FI).</p> <p>(74) Agent: FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: ARRANGEMENT, EQUIPMENT AND METHOD FOR TESTING HETEROGENEOUS CATALYSTS FOR SHORT CONTACT TIME REACTIONS</p>		
<p>(57) Abstract</p> <p>This invention relates to an arrangement, equipment and method for testing heterogeneous catalysts for short contact time reactions. It is a novel application of capillary technique where capillary tubing and separation columns are used as on-line sampling probes as well as for separation of compounds. The equipment comprises a furnace which gives a broad and uniform temperature profile, a tube reactor, adapter units, gas and liquid injection valves, a gas chromatograph furnished with suitable detectors, mass-flow and temperature measurement controllers, an injector, a reactor and column head pressure adjusting valve, an on-line sampling application with capillary technique, with splitting of sample with capillary technique, simultaneous detection of pulse mode, hydrogen and compound responses.</p>		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Arrangement, Equipment and Method for Testing Heterogeneous
Catalysts for Short Contact Time Reactions

5

This invention relates to an arrangement, equipment and method for testing catalysts for short contact time reactions. It is a novel application of capillary technique where capillary tubing and separation columns are used as on-line sampling probes as well
10 as for separation of compounds. The equipment is feasible for testing catalysts and catalytic reactions with short contact times, it is operated by pulse method and the products are analysed preferably using on-line gas chromatography.

Product yields of catalytic cracking, coke combustion, regeneration of catalyst and
15 kinetic studies are usually evaluated from experiments carried out in fixed bed tube reactors. The feed times are long, often tens of seconds, which means that the product distribution is an average value and that the performance of the catalyst is not stable due to coking of the catalyst. The accuracy in evaluation of the initial product distributions and the initial rates of the cracking reactions is diminished by
20 the average value and transient behaviour of catalyst activity. In addition, traditional laboratory testing methods such as micro activity method (MAT) ASTM D 3907-80, improved methods D 3907-87 and D 3907-92, could only be used within strictly limited reaction conditions, which are not sufficiently broad from reaction modelling point of view. Typically conventional methods applying cold trap without
25 capillary technique have been used. Continuously operating reactors are not suited for testing catalysis with short contact times and thus the only solution is a pulse reactor. The advantages of a pulse reactor for catalytic cracking experiments of different gas oils are that catalyst activity can be considered constant due to very short contact times and temperature can be considered constant due to small amount
30 of injected oil.

In regard to reaction modelling injection pulse of the feed should meet the catalyst as a plug flow mode and therefore mixing of feed with carrier gas should be avoided. The only way to prevent mixing of gases is to minimize dead volume between point of injection and catalyst. Mixing of gases will also increase the width of sample pulse and deteriorate the resolution of compounds. Possible alternatives to avoid loss of resolution in compound analysis is either to minimize dead volume between catalyst bed and separation column or to use liquid nitrogen trapping and flash evaporation.

There are several applications available using similar basic principles which are to connect the test reactor or furnace directly into the gas chromatograph (GC) described by *M.I. Yanovskii and A.D. Berman, (J. Chrom. 1972, 69, 3—15)* and to inject the feed into separate evaporator or injector or upper zone of reactor tube. In addition carrier gas is used to transport evaporated feed over catalyst and reaction products into separation column. Furthermore, same carrier gas acts also as an effluent gas in separation column. The main differences between the applications of the state of the art are the choice of furnace, separation column, sample trapping, splitting and detector alternatives.

An apparatus for pulse kinetic studies is presented by *R. Collyer, M. Larocca and H. de Lasa, (Can. J. Chem. Eng. 1989, 58, 513—516)*. In the experimental arrangement the reactor and thermal conductivity detectors (TCD) are connected in sequence so that the pulse of both the feed and of the products are measured. Products from reactor are trapped before separation column. Hydrogen response is not measured.

J.F. Coopmans, P. Mars and R.L. de Groot, (Ind. Eng. Chem. Res. 1992, 31, 2093—2103) have made pulse experiments of gas oil cracking on zeolitic catalyst with a pulse reaction unit connected to a packed column of GC. Oil pulses are measured directly without an analytical column. Because of broadening of the pulse in system, analytical resolution is deteriorated and for example ethane and ethylene can not be separated.

An application of commercial pyrolysis-gas chromatography (Py-GC) is an example of furnace alternatives. Pyrolysis-gas chromatography is well-known analysis technique for high molecular weight samples as well as for catalytic pyrolysis and for analysis of residues adsorbed on catalysts. Py-GC has also been applied for testing catalytic reactions of ethylbenzene over mid-pore zeolites by *G. Perez, M. Raimando, A. de Stefanis and A.A.G. Tomlinson, (J. Anal. Appl. Pyrol. 35 (1995) 157—166).*

Another Py-GC application by *M.I. Nokkosmäki, E.T. Kuoppala, E.A. Leppämäki and A.O.I. Krause, (J. Anal. Appl. Pyrol. 44 (1998) 193—204)* is a method for cracking of pyrolysis vapours of Scots pine sawdust with zeolites. In this method solid feed is pyrolysed with pyrolytic probe and vapour-phase is contacted with a catalyst loaded in the liner tube of injection port.

A Py-GC application is also presented in patent application WO 94/20848 which provides an improved sample injector for use in gas chromatography. The injector features an arrangement to allow a pyrolytic probe to be more easily inserted into the vaporization cavity while permitting the sample to be volatilized in such a way that the sample is more efficiently introduced onto the column.

In spite of numerous methods available not a single one is able to measure pulse of the feed, to separate compounds from C_1 to C_{20} and to detect hydrogen simultaneously. Typically GC-distillation has been performed which enables only the determination of compound groups, not individual compounds. Capillary technique is another technical feature that has not been utilised for on-line sampling in catalytic testing equipment of laboratory scale. A cold trap has always been used causing additional condensing and reevaporation steps. Therefore there clearly exists a need for a method and equipment for testing catalysts for short contact time reactions, which method is operated using large scale of temperature, wide catalyst to oil ratio and contact time for obtaining reliable data from catalytic reactions and from performance of catalysts.

The object of this invention is to provide an arrangement, equipment and method for testing heterogeneous catalysts for short contact time reactions and for testing catalytic reactions.

- 5 It is characteristic for the arrangement, equipment and method for testing heterogeneous catalysts for short contact time catalytic cracking, skeletal isomerization, hydrogenation, dehydrogenation and methane coupling reactions, what is presented in the claims.
- 10 The invention is a novel application of capillary technique. Pulse mode of injection, hydrogen response and analysis of hydrogen, hydrocarbon compounds from C_1 to C_{20} in products are detected simultaneously using flame ionisation (FID) and/or mass-selective and/or TCD and/or AED as detectors, and capillary tubing and separation columns are utilized as on-line sampling probes as well as for separation
- 15 of compounds. The equipment for testing catalysts according to the invention is herein abbreviated as ETC. The coke deposited on the catalyst is determined using well-known techniques by passing pulses of oxygen over catalyst and analysing amounts of products with on-line GC.
- 20 The arrangement and equipment according to the invention are well suited in testing and monitoring of heterogeneous catalysts, catalytic reactions, cracking reactions, skeletal isomerization reactions, measurements of catalyst deactivation, dehydrogenation, methane coupling and hydrogenation with short contact times. The equipment is operated by pulse method and the products are analysed for example by
- 25 on-line gas chromatograph. The equipment comprises preferably a furnace, a gas chromatograph furnished with suitable detectors, a tube reactor, gas and liquid injection valves, temperature measurement controllers, reactor and column head pressure adjusting valve, mass-flow controllers and an injector. For catalytic cracking tests gas oil is injected into the upper section of the reactor by generally
- 30 known means. The individual components and compounds can be separated conveniently using capillary columns. Any oils and gases with the boiling point equal or less than 550°C can be used as feedstock. The reactor can be operated within the

temperature range of 20—900°C depending on the feed, reaction and reaction circumstances, with wide catalyst to oil ratios and with residence times 0.01—0.1 s without losing resolution of compound separation. In connection with skeletal isomerization and oligomerization reactions when using feedstock comprising
5 $\geq C_4$ compounds, compound level resolution can be achieved with residence times 0.01—0.3 s. When using longer residence times up to 5.9 s compound level resolution is deteriorated and only GC-distillation results are obtained.

The equipment is preferably constructed by using commercial components and/or
10 components specially designed for the purpose. The major components are a furnace which gives a broad and uniform temperature profile, a tube reactor, preferably of glass, steel, other suitable metal, ceramic material or quartz, adapter units, gas and liquid injection valves, preferably six-way valves, a gas chromatograph furnished with a suitable detectors, such as flame ionisation (FID) and/or mass-selective and/or
15 TCD and/or AED and preferably FID and TCD, mass-flow and temperature measurement controllers, reactor and column head pressure adjusting valves, and an injector, preferably a semi-automatic one.

A preferred embodiment of the arrangement and equipment according to the invention,
20 tion, for testing catalysts and catalytic reactions with short contact time is provided in attached Figure 1.

In Figure 1 in the measurement arrangement the tube reactor 2 is connected into an injection port 36 of GC 20 with two special adapter units 29 and 16. In the first
25 adapter unit 29 there are six input holes for reactor 2, separation column 38, split-gas capillary inlet 14, split-gas outlet 13, temperature measurement probe 30 and pulse measurement and hydrogen sample capillary probe 31. The separation column 38 is inserted through the injector septum 19 and liner tube 37 and lifted up into the reactor tube 2 30 mm below the catalyst bed 5 with a specially constructed second
30 adapter 16. In this way separation column 38 can be used as a sample probe for on-line sampling as well as for separation of compounds. The reactor and injector are phase separated with gas-tight septum 17. The tip of thermocouple 7 is placed just

below the catalyst layer 5. The both adapter units 29 and 16 are heated to constant temperature (200 °C) with a heating block 10. The feed 24 is injected into the reactor 2, preferably either manually or using semi-automatic injector or gas or liquid injection valves and the compounds in the product which is analyzed are separated with a capillary column 38 and detected with FID 39. In the carrier gas line 23 a six-way valve or gas or liquid injection valves 22 and a sample loop can be used in the case of applying gaseous feed in tests. A TCD 26 is used as a pulse mode detector and another TCD 27 used for hydrogen detection, is placed in a coke measurement system. It is also used for detection of permanent gases and unreacted oxygen of the oxidizing pulse in catalyst regeneration. Additionally 1 represents manual injection block, 21 manual injection septum, 3 furnace, 4 and 6 quartz wool, 8 tip of sample probe, 9 tip of split-gas tube, 11 pressure release valve, 12 reactor and column head pressure adjusting valve, 13 split-gas outlet, 14 split-gas inlet, 15 split-gas tube, 18 replaceable needle-block, 28 tip of capillary column, 35 capillary column inlet needle, 23 carrier gas inlet, 32 pulse measurement mass-flow controller, 25 pulse and hydrogen measurement mass-flow controller, 33 molecular sieve, 31 sample probe inlet and 34 mode selection valve. The correct order of tips 7,8 and 9 is essential for sampling.

In the following is provided a brief description of principles of action and preferable embodiments related to the arrangement according to the invention. A microscale reactor has a threefold mode of action. It operates simultaneously as a vaporiser or injector, a reactor and a sample splitter. The upper section of the reactor acts as a vaporising zone where liquid feed is evaporated. Carrier gas transports the vaporized feed into the middle zone of the reactor where it is in contact with the catalyst and reactions occur. Using capillary technique the lower zone of reactor tube may be converted to a sampling area where the tip of sample probe for pulse measurement and hydrogen analysis is located just below the catalyst. Splitting of product gas between pulse measurement and compound analysis can be adjusted with mass-flow controller connected to the outlet of TCD. Downstream after sampling probe the product gas is diluted with extra helium gas flow with a split-gas capillary. A sample for compound analysis is taken from the diluted product flow using second sampling

probe. The reaction zone is located at the most uniform area of the temperature profile of the furnace. During test runs the residence time of feed over catalyst is controlled with carrier gas flow rate and the split-ratio with split-gas flow rate. The pressure of the reactor and the effluent gas flow rate are adjusted with column head
5 pressure regulator which is connected to split-gas outlet line.

In the experiments tube reactors have been utilized. In the middle of the reactor there is a funnel-shaped restriction where a layer of quartzwool or other suitable material is placed in order to adjust the position of catalyst. The reactor is cleaned
10 from contaminants by flushing it with oxygen pulses at the same temperature where the regeneration was carried out. Suitable amount of catalyst is 0.01—300 mg and it is loaded in the middle of the tube reactor, in the zone where the temperature profile of the furnace is most uniform.

15 For catalytic cracking tests gas oil is injected into the upper section of the reactor manually or with a semi-automatic injector. For gaseous feed gas loop is preferably used for injection. If the boiling range of the feed is low enough, for example 100—150 °C, liquid injection valve may also be used.

20 In the equipment according to the invention a capillary column is used as a sample probe for on-line sampling as well as for separation of compounds. The tip of the separation column is placed approximately 15 mm below the tip of split-gas capillary. Split ratio and delay time in sampling zone are adjusted with split-gas flow. Due to small dead volume in the sampling area a temperature program with
25 starting temperature 0 °C (2 min) and rate speed of 1.5 °C/min to the final temperature of 300°C is a preferable and proper method to achieve resolution of compounds from C₁ to C₂₀.

The amount of coke can be measured for example with a pulse method using
30 separate equipment. Calculation of the coke amount is based on external calibration carried out in the same way using coke samples as reference, the amount of coke of which is analyzed using commercially available methods.

The lowest possible operating temperature of the reactor depends on the boiling range of the oil. The liquid feed is vaporised in the beginning of the catalyst/inert bed which allows gas phase reactions. The volatilisation of the liquid feed is ensured by high mass-ratio between the catalyst/inert bed and the feed, also the temperature drop in consequence of the volatilisation is very small. Gas phase feed to the reactor is also possible. The highest operating temperature is restricted to the temperature of 900 °C.

The feedstock may be any kind of liquid or gas feed with the boiling point equal or below 550 °C. The viscosity of the liquid phase feedstock must be low enough to ensure uniform injection. In the case of high viscosity at room temperature the feed must be heated to a sufficient temperature. The amount of the feed can be varied in the range of 0.1—1.0 μl without loss of resolution or stability of temperature.

Any kind of heterogeneous catalysts may be used in experiments and testing. The maximum length of the catalyst bed is restricted to 30 mm because of the temperature profile of the heating oven. The temperature profile in the region of the catalyst bed should be as flat as possible in order to ensure uniform temperature in the bed and therefore uniform conditions for the reactions.

The catalyst to oil ratio can be varied within a wide range of 0—300. For example, when the density of the feed is 780 kg/m^3 and the volume of the injected oil is 0.5 μl (0.43 mg) the catalyst to oil ratio may be in the range of 0—45 $\text{g}_{\text{cat}}/\text{g}_{\text{oil}}$ with diameter of the reactor 2 mm. The length or volume of the catalyst/inert bed is always kept constant, only the mass fraction of the catalyst in the bed is varied.

The residence time of the feed in the catalyst can be controlled indirectly by varying the flow rate of the carrier gas through the reactor. The flow rate of the carrier gas may be varied between 0.1—83.3 cm^3/min (NTP), which corresponds to the residence times of 0.01—5.9 s, at 600 °C, bed volume 22.9 cm^3 of the carrier gas.

As a preferable embodiment of the invention one variation of the test method is described in the following.

5 The first step in the test method is to load a known amount of catalyst into the tube reactor. After loading the reactor is connected to the adapter unit of test equipment and the furnace is placed onto the reactor so that location of the catalyst layer is in the middle of uniform temperature profile of the furnace. The carrier gas line with manual injection block is connected to the upper end of the reactor and the reactor is flushed with carrier gas through pressure release valve. The carrier gas flow rate, 10 split ratio and sample splitting between capillary column and pulse mode measurement are adjusted with mass flow controllers. Reaction pressure is adjusted manually with a needle valve connected to the split gas outlet. After test temperature has exceeded the value of setting point and stabilised and the pre-treatment steps of catalyst are carried out the test reaction is started by manual or sample loop injection 15 of the feed into the reactor. After analysis of products is finished the reactor tube including coked catalyst is removed from test unit and connected to the adapter unit of coke measurement equipment. The amount of coke deposited on the catalyst is measured with pulse method (pulses of oxygen/helium mixture) using a suitable highly sensitive method, for example methanation for detection of carbon-monoxide and carbon-dioxide as methane. Analytical instruments are controlled and data is 20 collected with commercial soft-ware using a personal computer. Hydrogen and coke amounts are calculated using external calibration.

25 MAT-equipment is commercial equipment suited for the comparison of different FCC (Fluid Catalytic Cracking) catalysts for catalytic cracking of heavy hydrocarbons. According to the invention the combination of a reactor and an oven with a GC in testing of catalysts for the catalytic cracking reactions gives several superior features compared to MAT with respect to the process variables and analytical techniques.

30

In MAT-equipment, the gas phase sample is collected to a gas pipette during the experiment and the liquid phase sample is separated as a condensate. Therefore two

separate analyses are needed. Furthermore, the samples of average nature are collected during rather long reaction time (20—75 s), while the activity of the catalyst declines during the experiment due to coking. With the ETC-equipment according to the invention the product gas is splitted to two sample flows with capillaries and analysed simultaneously and thus pulse mode, hydrogen response and compound analysis are obtained. Further, because of the very short contact time the catalyst maintains its activity during the experiment.

In testing catalyst performance several variables, for example temperature, catalyst to oil ratio, residence time and cumulative amount of the feed are used. In the ETC-equipment these variables may be varied in considerably larger ranges than in MAT. In the ETC-equipment the lowest possible temperature for the liquid feeds is determined by the boiling point of the feed and for the gas feeds temperature may be lower than 100 °C. For example, for a gas oil feed the temperature may be between 20—900 °C. Catalyst to oil ratio may be from zero to 300. The residence times may be varied by adjusting carrier gas and split gas volume flows, in the equipment according to the invention the range of the residence times is usually from 0.01 s to 0.1 s. In connection with skeletal isomerization and oligomerization reactions, when using feedstock comprising $\geq C_4$ compounds, compound level resolution can be achieved with residence times 0.01—0.3 s. The volume of the liquid feed injected may be varied in the range of 0.1—1.0 μ l without having any problems with temperature control.

In addition, the regeneration of the catalyst after the cracking reactions may be carried out by pulse method. The cumulative amount of the coke formed during the reaction is obtained by summing up the formed CO and CO₂. By feeding a fixed volume of air in one pulse with known residence time the kinetics of the coke combustion may also be evaluated by analyzing the formed CO and CO₂ after each pulse. In commercial MAT-equipment the catalyst is regenerated after the experiment and the cumulative CO₂ amount is analyzed by IR-detector. In ETC-equipment CO and CO₂ are first converted to methane and then analyzed by FID which is several orders of magnitude more sensitive method than IR. By FID less than 0.1 μ g

of coke may be analyzed, which correspond to the coke fraction of less than 0.025 wt% in the catalyst. In addition, regeneration in MAT doesn't give any additional information about the coke combustion kinetics. Major features of the ETC- and MAT -equipment are summarized in Table 1.

5

Table 1. Major features of ETC- and MAT-equipment.

Feature	ETC	MAT (ZETON)
Temperature range	From the 20 to 900 °C	From RT to 650 °C
10 C/O ratio	0—300	0—20
Residence time	0.01—0.3 s	20—75 s
Phase of the feed	Liquid or gas	Liquid
Mass of the catalyst	0—300 mg	5—6 g
Sample	Instantaneous	Average
15 Coke analysis	Pulse method, CO and CO ₂	Cumulative CO ₂

The advantages of this kind of reactor for catalytic cracking experiments are that the catalyst activity may be considered to be constant due to very short contact times and the temperature may be considered to be constant due to small amount of injected oil. The reproducibility of the experiments was shown to be excellent.

The preferred embodiments according to the invention are presented in the following as examples which are not meant to limit the scope of the invention. Preferred modifications of the method according to the invention are provided in the following as examples 1—5.

Example 1

Thermal Cracking

5 Thermal cracking was studied by filling the reactor with 20 mg of inert material (Inert Microspheres MS-3X, same material was used with the catalysts to get the needed catalyst amount in the bed) and with quartz wool. The reactor material was quartz glass and the feed a light gas oil with boiling range between 221—420 °C (96 %, gas oil 1). The experiments were conducted as a function of temperature
10 between 500—700 °C, the residence times of the carrier gas were constant ($t = 0.055$ s, $Re_p = 5$) and the amount of feed was 0.5 μ l (0.43 mg). The product distribution was pooled to five different groups, namely converted feed (< 221 °C), yields of gasoline (C_5 -221 °C) (kg/100kg of feed), liquified petroleum gas (LPG C_3 - C_4), dry gases (C_1 - C_2) and coke. The results of these experiments are
15 shown in Table 2.

Table 2. Conversion and yields of thermal cracking of gas oil 1.

		Conversion/Yields				
		Conversion	Dry Gases	LPG	Gasoline	Coke
20	Temperature/°C					
	500	3.6	0.07	0.13	3.34	0.04
	500	3.6	0.07	0.23	3.30	0.11
	550	4.2	0.24	0.43	3.53	0.03
25	550	6.0	0.22	0.45	5.26	0.09
	600	9.2	1.17	1.30	6.51	0.23
	600	10.0	1.06	1.09	7.79	0.05
	650	32.4	6.83	6.99	18.5	0.09
	650	30.0	6.15	6.41	17.2	0.20

30

According to the results thermal reactions are negligible below the temperature of 600 °C. Therefore, in order to study the catalytic reactions alone it is favorable to keep the temperature below this value. However, thermal cracking is always

associated with catalytic cracking and the separation of these two phenomena is difficult because of the complexity of the interactions between the molecules involved in these reactions.

5 Example 2

Catalytic Cracking

Catalytic cracking experiments were carried out as a function of temperature, catalyst to oil ratio and residence time. The gas oils used were light gas oil with boiling range between 221—420 °C (96 %, gas oil 1) and 227—530 °C (96 %, gas oil 2). Temperature was varied between 400—650 °C, catalyst to oil ratio between 0—29.8 and residence time between 0.03—0.09 s. The amount of injected oil was always 0.5 μ l (0.43 mg) and the catalysts and zeolites used were commercial equilibrium catalysts and zeolite catalysts containing rare earth elements.

Experiments by varying the bed temperature were carried out with the catalyst to oil ratio of 11.2 and with the residence time of 0.055 s. Results of these experiments as a function of temperature are shown in Tables 3—5. Results of cracking of gas oil 1 as a function of catalyst to oil ratio over equilibrium catalyst are provided in Table 6, and results of catalytic cracking of gas oil as a function residence time are presented in Table 7.

15

Table 4. Conversion and yields of catalytic cracking of gas oil 1 as a function of temperature over zeolite catalyst containing rare earth elements.

		Conversion/Yields				
		Conversion	Dry Gases	LPG	Gasoline	Coke
5	Temperature/°C					
	400	43.0	0.07	7.4	35.1	0.5
	400	44.0	0.08	7.0	36.1	0.8
	450	55.6	0.15	10.7	43.9	0.8
	450	50.1	0.20	10.3	47.6	0.9
10	500	74.9	0.41	17.6	56.0	0.9
	500	68.4	0.39	15.0	52.2	0.8
	500	74.0	0.38	15.9	57.0	0.7
	550	79.4	0.91	21.6	55.9	0.8
	550	79.3	0.84	21.0	56.8	0.7
15	600	85.2	2.88	29.5	51.3	1.5
	600	84.3	2.01	28.0	52.5	1.8
	650	84.6	6.89	32.9	43.1	1.8
	650	87.6	8.78	35.8	39.6	3.4

20

According to the above presented results zeolite catalysts containing rare earth elements are clearly more active when compared to equilibrium catalysts. Conversion of cracking reaction is 15—20 higher over the whole temperature scale and the maximum yield of gasoline is obtained at 550 °C.

25

Table 5. Conversion and yields of catalytic cracking of gas oil 2 as a function of temperature over equilibrium catalyst.

		<i>Conversion/Yields</i>				
		<i>Conversion</i>	<i>Dry Gases</i>	<i>LPG</i>	<i>Gasoline</i>	<i>Coke</i>
5	450	49.0	0.12	10.9	37.5	0.5
	450	57.0	0.15	11.9	43.9	1.1
	450	53.5	0.13	11.2	41.3	0.9
	500	62.5	0.30	13.7	47.3	1.3
10	500	60.0	0.28	13.4	45.6	0.7
	550	71.9	0.74	16.9	53.4	0.9
	550	71.0	0.73	17.2	52.2	0.8
	600	79.3	2.14	24.0	51.8	1.4
15	600	78.4	1.92	23.9	50.9	1.7
	650	85.4	7.69	28.8	46.9	2.0
	650	84.8	6.97	27.8	48.6	1.4

Based on the results cracking of gas oil 2 occurs more easily than cracking of gas oil 1 over equilibrium catalyst. The yields of different groups follow same logical trends in both cases as a function of temperature with the exception that the yields are higher for gas oil 2.

Experiments as a function of catalyst to oil ratio were carried out by varying the amount of catalyst in inert material. The catalyst mass in the bed varied between 4.0—34.4 wt% and the catalyst bed volume was constant. The temperature in these experiments was 550°C and the residence time was 0.055 s, which gave the particle Reynolds number of 6.6. The results are shown in Table 6.

Table 6. Conversion and yields of catalytic cracking of gas oil 1 as a function of catalyst to oil ratio over equilibrium catalyst.

		<i>Conversion/Yields</i>				
	<i>Catalyst to oil ratio</i>	<i>Conversion</i>	<i>Dry Gases</i>	<i>LPG</i>	<i>Gasoline</i>	<i>Coke</i>
5	0	4.2	0.24	0.4	3.5	0.03
	0	6	0.22	0.5	5.3	0.09
	2.6	19.4	0.34	3.6	14.6	n.d.
	2.6	20.7	0.15	3.3	15.8	n.d.
10	5.5	28.6	0.37	6.1	21.8	0.4
	5.5	30.7	0.34	6.2	23.7	0.5
	8.1	36.8	0.34	8.3	27.9	0.3
	8.1	39.1	0.45	8.4	29.8	0.5
	11.2	50.4	0.54	12.3	36.7	0.9
15	11.2	54	0.51	13.2	39.9	0.5
	11.2	54.4	0.65	13.4	39.5	0.8
	11.2	52.2	0.53	12.9	38.2	0.6
	13.5	55.9	0.5	13.5	41.2	0.7
	13.5	58.4	0.62	14.7	42.1	1
20	13.5	58.4	0.66	14.3	42	1.5
	15.9	68.4	0.91	19.4	47.2	0.9
	15.9	64.7	0.78	17.5	45.4	13.5
	15.9	63	0.77	17.5	43	13.5
	15.9	65.5	0.77	19.7	44.1	13.5
25	20.3	74.5	0.98	21.8	50.1	15.9
	20.3	64.3	0.76	17.6	44.3	15.9
	20.3	68.6	0.8	19	47.9	15.9
	25.2	76.4	0.98	22	52	1.5
	25.2	72.3	0.91	21	48.3	2.1
30	29.8	79.3	1.11	24.1	51.5	2.5
	29.8	74.6	1.04	22.5	49.6	1.5

The conversion and yields of gasoline and LPG increase strongly with growing catalyst to oil ratios after which they begin to flatten out. Again increase of yields of dry gas and coke are nearly linear within this range of catalyst to oil ratio.

Residence times were varied between the values of 0.03–0.09 s by controlling the flow rates of the carrier gas. The corresponding particle Reynolds numbers were between 4.1–12.6. Again, the experiments were carried out at the temperature of 550°C with the catalyst to oil ratio of 11.2. The results as a function of residence time are shown in Table 7.

Table 7. Conversion and yields of catalytic cracking of gas oil 1 as a function of residence time.

		Conversion/Yields				
	Residence time/s	Conversion	Dry Gases	LPG	Gasoline	Coke
15	0.0	4.2	0.24	0.4	3.5	0.03
	0.0	6.0	0.22	0.5	5.7	0.09
	0.03	38.8	0.36	8.1	29.9	0.5
	0.03	41.3	0.36	9.1	31.2	0.7
20	0.055	50.4	0.54	12.3	36.7	0.9
	0.055	54.0	0.51	13.2	39.9	0.5
	0.055	54.4	0.65	13.4	39.5	0.8
	0.055	52.2	0.53	12.9	38.2	0.6
	0.070	57.9	0.72	14.8	41.8	0.6
25	0.070	59.7	0.73	16.2	41.9	0.9
	0.090	62.9	0.78	16.4	44.8	0.9
	0.090	58.3	0.77	15.7	40.9	0.9

30 The conversion and the yields of different groups increase as the residence time increases. With long residence times the conversion and the yields start to flatten out, which is a symptom of mass transfer limitations to the reaction rate. Indeed,

with the longest residence time of 0.09 s, the particle Reynolds number is 4.1 which appears to be too low value to ensure that the kinetic rate controls the overall rate.

Example 3

5

Skeletal Isomerization

Skeletal isomerization experiments were carried out as a function of temperature using constant catalyst to oil ratio (60) and residence time (0.23 s). The feed was light gas oil containing n- and i-paraffins, n- and i-olefins with boiling range between 47—97 °C (96 %). Temperature range was varied between 275—350 °C. The amount of injected oil was always 0.5 µl (0.43 mg) and the catalyst used was ferrierite catalyst. Results of these experiments are presented in Table 8.

15 **Table 8.** Conversion and yields of skeletal isomerization of light oil as a function of temperature.

		Conversion of n-olefins/Yields				
Temperature/°C		Conversion	n-Paraffins	i-Paraffins	n-Olefins	i-Olefins
20	275	50.8	9.34	46.8	9.61	22.1
	275	47.0	9.29	49.1	10.4	19.5
	300	40.1	9.37	46.6	11.7	20.7
	300	43.8	9.95	48.3	11.0	18.0
	325	35.6	9.60	48.3	12.6	16.9
25	325	33.5	9.90	48.4	13.0	16.5
	350	25.9	9.85	46.5	14.5	16.4
	350	20.2	9.59	47.7	15.6	15.1

According to the results the yields of different products follow a logical trend as the temperature rises: Conversion of n-olefins decreases and selectivity to i-olefins decreases due to the increasing activity of side-reactions. Consequently lower temperature is favourable for i-olefin selectivity and yield. It also can be noted that the type of reaction, type of catalyst and feed have influence on the residence time.

Example 4**Dehydrogenation tests**

- 5 Dehydrogenation experiments were carried out as function of temperature using constant catalyst to feed -ratio and residence time (0.055 s). The feed was n-butane gas (99.7 %). Temperature range was varied between 400—475 °C. The amount of injected gas was always 500 μ l and the catalyst used was a dehydrogenation catalyst. Results of these experiments are presented as mole-% in Table 9.

10

Table 9. Conversion and yields of dehydrogenation of n-butane as a function of temperature.

15	Temperature/°C	Conversion of n-butane/Yields				
		Conversion	n-Butane	C ₄ -Olefins	Hydrogen	Others
	400	3.7	96.3	1.8	1.5	0.5
	400	3.5	96.5	1.7	1.3	0.5
	425	4.9	95.1	2.5	1.9	0.4
	425	5.0	95.0	2.6	2.0	0.5
20	450	9.1	91.0	4.8	3.8	0.5
	450	8.7	91.3	4.6	3.7	0.5
	475	11.9	88.1	6.4	5.1	0.5
	475	12.0	88.0	6.4	5.2	0.5

25

According to the results the yields of olefins follow a logical trend as the temperature rises: conversion of n-butane increases and selectivity to olefins and hydrogen increases due to increasing activity of catalytic reactions.

30

Example 5

Deactivation of cracking catalyst

- 5 Deactivation of cracking catalyst was studied by repeating the injection step several times (1, 2, 3, 10, 20 and 30) at the same conditons and taking samples into compound analysis from the last injection. Experiments were carried out at tempera-
ture of 600 °C, catalyst to oil -ratio 11.2 and residence time 0.055 s. The feed oil
was light gas oil with boiling range between 221—420 °C (96 %, gas oil 1). The
10 amount of injected oil was always 0.5 μ l (0.43 mg) and the catalysts used was commercial zeolite catalyst containing rare earth elements. Scale of time on stream was 0.055—1.65 s. Cumulative amount of coke was measured after each test and final coke amount was calculated as a difference between last two injections from measured cumulative results. The cumulative results are shown in Table 10 and final
15 results are shown in Table 11.

Table 10. Conversion and yields of catalytic cracking of gas oil 1 as a function of time on stream over zeolite catalyst containing rare earth elements.

	<i>Injections/Time on stream/s</i>	<i>Conversion/Yields</i>				
		<i>Conversion</i>	<i>Dry Gases</i>	<i>LPG</i>	<i>Gasoline</i>	<i>Cumulative amount of Coke</i>
5	1/0.055	90.8	3.3	34.5	49.9	3.1
	1/0.055	90.7	3.1	33.8	52.7	1.1
	1/0.055	88.4	3.6	33.1	48.9	2.7
10	2/0.11	91.0	2.9	32.7	52.5	3.0
	2/0.11	88.6	2.3	30.7	53.1	2.5
	3/0.165	88.0	2.9	30.1	49.8	5.3
	3/0.165	89.5	4.1	32.6	47.8	5.0
	10/0.55	88.5	2.3	26.5	54.1	5.6
15	10/0.55	87.8	4.1	27.0	49.7	7.1
	20/1.10	87.3	2.2	23.8	53.2	8.1
	20/1.10	86.8	2.3	23.6	53.2	7.7
	30/1.65	86.7	2.3	23.5	52.4	8.5
	30/1.65	83.8	2.2	20.6	52.6	8.3
20						

The cumulative amount of coke increases as a function of time on stream and the deactivation of catalyst can be seen as a decrease of conversion and LPG-yield.

Table 11. Conversion of yields of catalytic cracking of gas oil 1 as a function of time on stream over zeolite catalyst containing rare earth elements.

	<i>Injections/Time on stream/s</i>	<i>Conversion/Yields</i>				
		<i>Conversion</i>	<i>Dry Gases</i>	<i>LPG</i>	<i>Gasoline</i>	<i>Coke</i>
5	1/0.055	90.7	3.3	34.8	50.0	2.3
	1/0.055	90.8	3.1	33.4	52.1	2.3
	1/0.055	88.3	3.7	33.3	49.2	2.3
	2/0.11	90.9	2.9	33.3	53.4	1.3
10	2/0.11	88.4	2.3	31.1	53.8	1.3
	3/0.165	87.5	3.1	31.5	52.1	0.75
	3/0.165	89.1	4.3	34.0	50.0	0.75
	10/0.55	87.8	2.5	28.0	57.2	0.19
15	10/0.55	86.9	4.4	28.9	53.4	0.19
	20/1.10	86.2	2.4	25.9	57.9	0.09
	20/1.10	85.7	2.5	25.5	57.6	0.09
	30/1.65	85.5	2.5	25.6	57.3	0.06
	30/1.65	82.3	2.4	22.5	57.4	0.06

20

Based on the results the formation of coke in course of deactivation decreases. For instance, the yield of coke during first 0.055 is 2.25 wt% but after the activation period (1.6 s) on stream formed amount of coke is only 0.06 wt%.

Claims

1. An arrangement for testing heterogeneous catalysts for short contact time reactions, **characterized** in that it comprises
- 5 a furnace (3) which gives a broad and uniform temperature profile consisting of a tube reactor (2),
- adapter units (16,29) for through output of capillary column and connection of
- 10 reaction tube, split-gas capillary inlet, split-gas outlet, temperature measurement probe, pulse measurement and hydrogen sample capillary probe, by which volume of product gas chamber is controlled,
- an injection valve of feeding gas or feeding liquid (22),
- 15 a gas chromatograph (20) furnished with suitable detectors (26,27,39),
- mass-flow and temperature measurement controllers (25,32),
- 20 an injector (36), a reactor (2) and a column head pressure adjusting valve (12),
- on-line sampling application devices (8,9,28) with capillary technique with sample splitting, and
- 25 simultaneous detection of pulse mode (26), hydrogen (27) and compound responses (39).
2. An arrangement according to claim 1, **characterized** in that a residence time in the range of 0.01—0.3 s is used.
- 30 3. An arrangement according to claim 1 or 2, **characterized** in that a residence time in the range of 0.01—0.1 s is used.

4. An arrangement according to any of claims 1—3, **characterized** in that scale of catalyst to oil ratio in the range of 0—300 is used.
5. An arrangement according to any of claims 1—4, **characterized** in that scale of temperature in the range of 20—900°C is used.
6. An arrangement according to any of claims 1—5, **characterized** in that oils and gases with the boiling point equal or below 550°C are used as feedstock.
7. An arrangement according to any of claims 1—6, **characterized** in that the injection volume ranges within 0.1—1.0 μ l.
8. Method for testing heterogeneous catalysts for short contact time reactions, **characterized** in that it comprises:
- loading the catalyst into a tube reactor (2), then connecting the reactor (2) to an adapter unit (29) of test equipment, placing a furnace (3) onto the reactor, connecting a carrier gas line (23) with injection block to the upper end of the reactor (2) and flushing the reactor (2) with the carrier gas,
- adjusting the carrier gas flow rate, split ratio and sample splitting between capillary column and pulse mode measurement and reaction pressure,
- after test temperature has exceeded the value of setting point and stabilized and optional pre-treatment steps of catalyst are carried out, starting the test reaction by sample injection of the feed into the reactor,
- controlling analytical instruments and collecting data and calculating hydrogen and carbon amounts.

9. Method for testing heterogeneous catalysts for short contact time catalytic cracking, skeletal isomerization, hydrogenation, dehydrogenation and methane coupling reactions, **characterized** in that it comprises:

5 loading the catalyst into a tube reactor (2), then connecting the reactor (2) to an adapter unit (29) of test equipment, placing a furnace (3) onto the reactor, connecting a carrier gas line (23) with injection block to the upper end of the reactor (2) and flushing the reactor (2) with the carrier gas,

10 adjusting the carrier gas flow rate, split ratio and sample splitting between capillary column and pulse mode measurement and reaction pressure,

after test temperature has exceeded the value of setting point and stabilized and optional pre-treatment steps of catalyst are carried out, starting the test reaction by

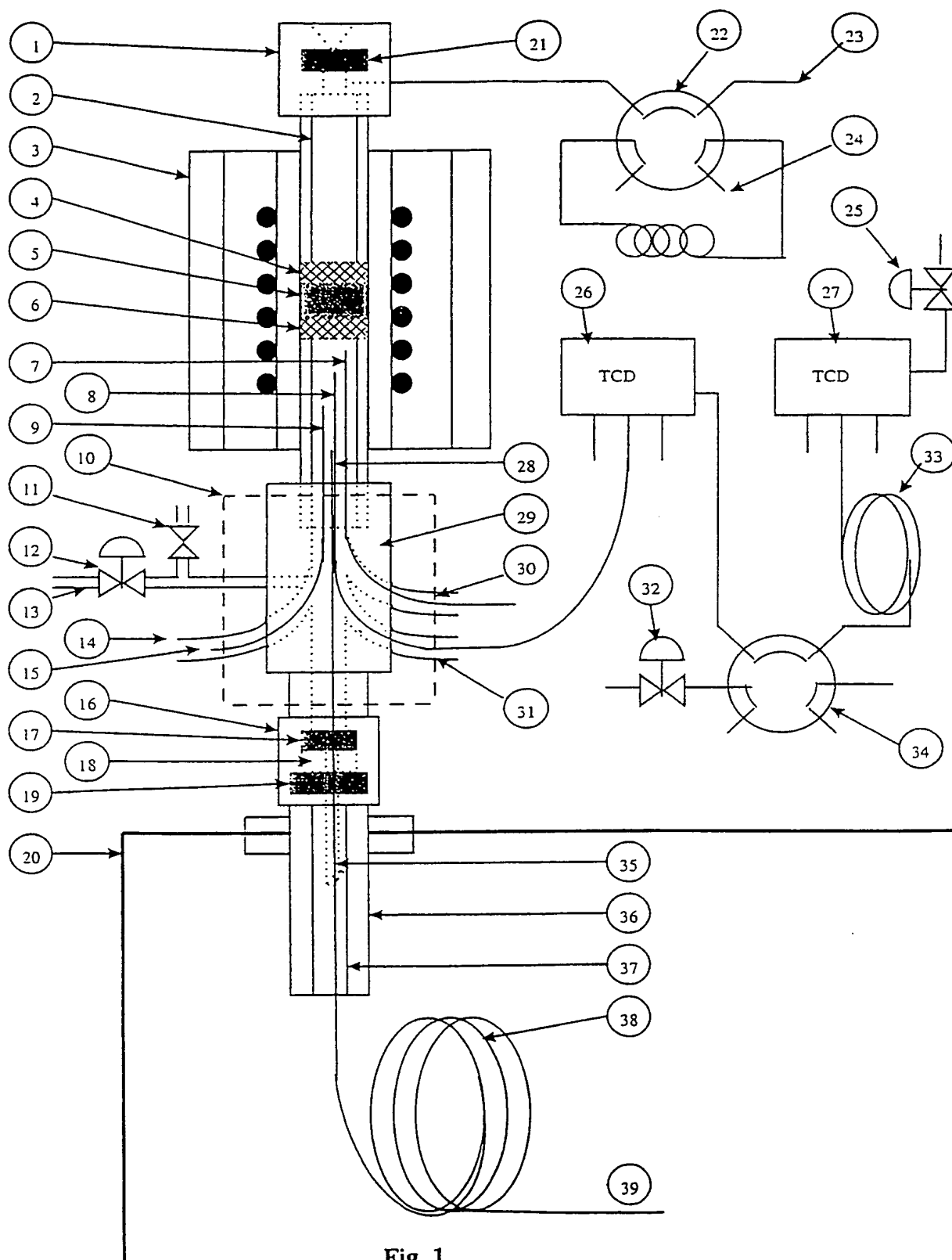
15 sample injection of the feed into the reactor,

controlling analytical instruments and collecting data and calculating hydrogen and carbon amounts.

20 10. Method according to claim 8 or 9, **characterized** in that hydrogen and C_1 - C_{20} hydrocarbons are detected.

11. Method according to claim 8, 9 or 10, **characterized** in that after the analysis the reactor tube (2) including the coked catalyst from the test unit is removed and

25 connected to the adapter unit of coke measurement equipment, the amount of coke deposited on the catalyst is measured with pulse method using a suitable highly sensitive method for detection of carbon monoxide and carbon dioxide as methane.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00382

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 31/10, G01N 30/88
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 62223669 A (NISSEI SOFTWARE KK et al) 1987-10-01 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 1999-08-27). Retrieved from: EPO WPI Database. DW 9514. Accession Number 95-104491 & JP 62223669 (NISSEI SOFTWARE KK) 1988-03-24 (abstract). (online) (retrieved on 1999-08-27) Retrieved from: EPO PAJ Database. figur 1, abstract --	1-11
A	GB 2124369 A (INSTITUT FRANCAIS DU PETROLE), 15 February 1984 (15.02.84), page 1, line 40 - line 43, claim 1, abstract --	1-11

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

31 August 1999

Date of mailing of the international search report

01 September 1999 (01.09.99)

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Moa Emiling/MP
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00382

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Ind.Eng.Chem.Res, Volume 31, 1992, Jo F. Coopmans et al, "Kinetics of Vacuum Gas Oil Cracking on a Zeolitic Catalyst", page 2093 - page 2103, figure 1 --	1-11
A	Journal of Analytical and Applied Pyrolysis, Volume 44, 1998, M.I. Nokkosmäki et al, "A Novel test method for cracking catalysts", page 193 - page 204, see page 194, 3rd, part -- -----	1-11

Information on patent family members

02/08/99

PCT/FI 99/00382

Form PCT/ISA/210 (patent family annex) (July 1992)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.